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Thermal emission spectrum of MnS molecule

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Abstract : Thermal emission spectrum of MnS molecule has been recorded in the spectral region $\lambda\lambda$ 4200-5900 Å at a reciprocal linear dispersion of 7.3 Å/mm using graphite tube furnace. The study reveals the presence of two band systems viz. A—X and B—X. The vibrational analysis has been carried out and it is suggested that both the systems arose from the ground state with the vibrational constant $\omega_e'' = 490.6$ cm^{-1}

Keywords : Thermal emission spectra, vibrational analysis, MnS molecule.

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1. Introduction

Preliminary communication about the emission band spectrum of MnS molecule was first made by Monjajeb and Mohon [1] in the spectral region $\lambda\lambda$ 4200-5900 Å. They classified the recorded bands into two systems viz. $\lambda\lambda$ 4200-4750 Å and $\lambda\lambda$ 4900-5890 Å. However the analysis is based on the spectrogram taken under the low dispersion (12-40 Å/mm) with Hilger E-492 Spectrograph. Biron *et al* [2] recorded the thermal emission spectrum of MnS molecule in the spectral region $\lambda\lambda$ 4900-6000 Å and identified the similar constants. Recently Doubay *et al* [3,4] reported rotational constants by investigating the rotational structure.

The present paper presents the detailed vibrational analyses of both the systems : A-X and B-X in the spectral region $\lambda\lambda$ 4200-5900 Å.

2. Experimental

A small quantity of an intimate mixture of pure manganese metal powder and sulphur or zinc sulphide or cadmium sulphide of spectroscopic grade was placed inside the graphite tube of the furnace described by Saha *et al* [5]. After making necessary routine adjustments, argon gas was filled at about a pressure of 50 cm of mercury. The spectrum has been photographed in the first order of Plane Grating Spectrograph (PGS-2) with a grating blazed at λ 5600 Å and total lines ruled 45600 at a reciprocal linear dispersion of 7.3 Å/mm. The exposure time of about six minutes was found sufficient to record good spectrogram on INDU 125 ASA black and white film. Iron dc are served the purpose of Comparison. The measurements were performed using Abbe Comparator with the least count of 0.0001 cm.

3. Results

Thermal emission spectrum of MnS molecule has been recorded in the spectral region $\lambda\lambda$ 4200-5900 Å and reproduced in the Figures 1 and 2. About 38 bands have been photographed and analysed into the two systems viz. A—X and B—X. All the bands are degraded to higher wavelength side. Out of the 38 bands, the system A—X consists of 26 while system B—X comprises 12 bands. A glance on the spectrogram shows that a part of the rotational structure has been resolved in some bands. The observed bands have been satisfactorily analysed yielding the following constants :

For A—X system

$$\omega'_e = 371.8 \qquad \omega_e' x_e' = 1.7 \text{ cm}^{-1}$$

$$\upsilon_{oo} = 18858.1$$

$$\omega''_e = 490.6 \qquad \omega_e'' x_e'' = 1.8 \text{ cm}^{-1}$$

For B—X system

$$\omega_e' = 466.7 \qquad \omega_e' x_e' = 2.1 \text{ cm}^{-1}$$

$$\upsilon_{oo} = 22319.8$$

$$\omega_e'' = 490.6 \qquad \omega_e'' x_e'' = 1.8 \text{ cm}^{-1}$$

We have also recorded a group of bands near the λ 4790 Å as reported by Doubay *et al* [3] and classified as (0, 3) sequence of the B-X system.

The band head data together with the visual estimates of intensities and their classifications are collected in Table 1. Table 2(a and b) represent the Deslandres' Scheme for the A—X and B—X systems respectively.

Table 1. Band head data of MnS molecule

υ_{cal} (cm^{-1})	υ_{obs} (cm^{-1})	(v', v'')		Int.	υ_{cal} (cm^{-1})	υ_{obs} (cm^{-1})	(v', v'')		Int.
					A—X System				
17407.9	17407.1	0	3	3	18739.5	18738.9	1	1	1
17300.1	17299.2	1	4	5	18621.1	18623.3	2	2	4
17192.5	17193.3	2	5	4	18502.9	18502.8	3	3	2
17887.7	17888.0	0	2	6	18384.9	18383.6	4	4	1
17776.3	17776.6	1	3	5	19226.5	19226.9	1	0	7
17665.1	17667.0	2	4	3	19104.5	19102.7	2	1	3
17554.1	17555.0	3	5	1	18982.7	18984.1	3	2	2
18371.1	18371.2	0	1	9	19591.5	19592.4	2	0	5
18256.1	18257.4	1	2	5	19466.1	19466.2	3	1	3
18141.3	18142.8	2	3	3	19340.9	19340.7	4	2	2
18026.7	18027.4	3	4	2	19953.1	19954.3	3	0	2
17912.3	17912.4	4	5	2	19824.3	19822.2	4	1	1
18858.1	18858.1	0	0	10	19695.7	19695.4	5	2	1

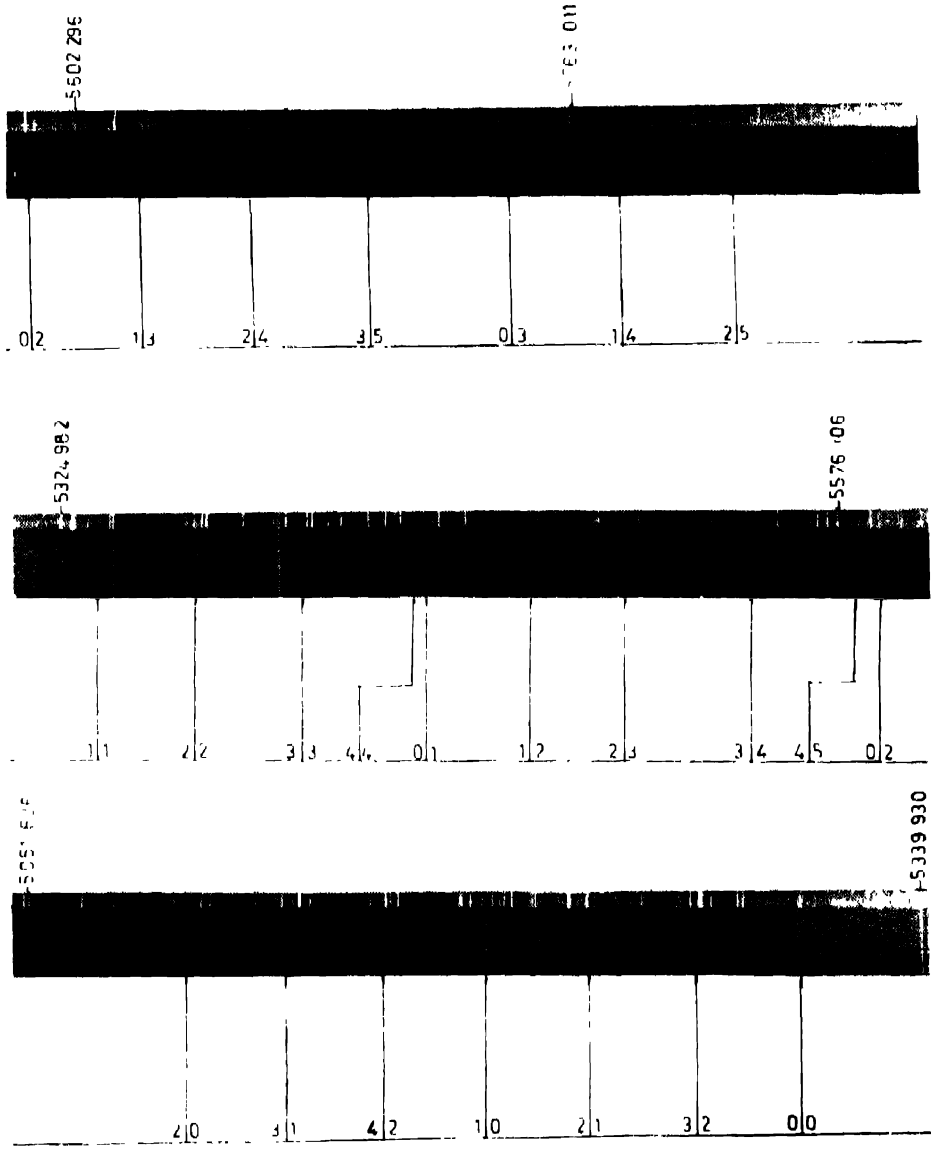

Figure 1. Thermal emission spectrum of A—X system of MnS molecule

Thermal emission spectrum of MnS molecule

Plate II

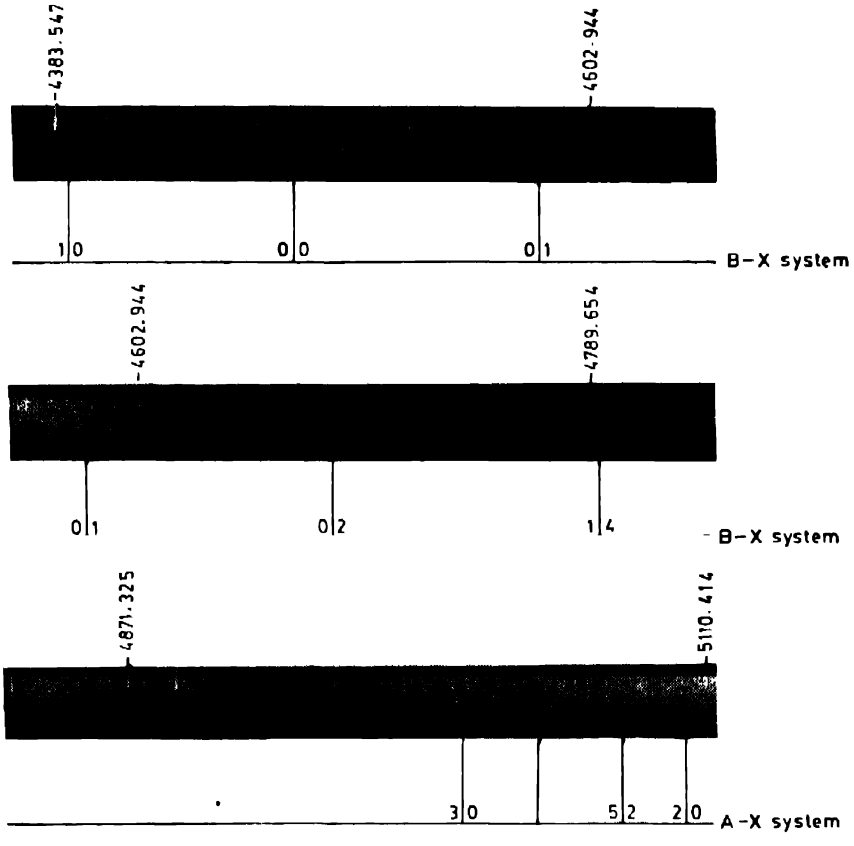

Figure 2. Thermal emission spectrum of B—X system of MnS molecule

Table 1.(*contd.*)

υ_{cal} (cm^{-1})	υ_{obs} (cm^{-1})	(v', v'')		Int	υ_{cal} (cm^{-1})	υ_{obs} (cm^{-1})	(v', v'')		Int.
					B-X system				
20855.9	20854.8	1	4	3	22724.3	22726.5	3	2	1
21349.4	21351.2	0	2	2	22753.6	22754.9	2	1	2
21832.8	21833.7	0	1	3	22782.3	22782.0	1	0	3
22270.2	22272.1	2	2	2	23207.7	23209.0	3	1	1
22295.3	22294.7	1	1	2	23240.6	23240.3	2	0	1
22319.8	22319.8	0	0	4	23694.7	23693.6	3	0	1

Table 2(a). Deslandres' scheme for the *A*—*X* system of MnS (Number in parentheses indicates visual estimates of intensity).

v'	0	1	2	3	4	5
0	18858.1 (10	18371.2 (9)	17888.0 (6)	17407.1 (3)		
1	19226.9. (7)	18738.9 (1)	18257.4 (5)	17776.6 (5)	17299.2 (5)	
2	19592.4 (5)	19102.7 (3)	18623.3 (4)	18142.3 (3)	17667.0 (3)	17193.3 (4)
3	19954.4 (2)	19466.2 (3)	18984.1 (2)	18502.8 (3)	18027.4 (2)	17555.0 (1)
4		19822.2 (1)	19340.7 (2)		18383.6 (1)	17912.4 (2)
5			19695.4 (1)			

Table 2(b). Deslanders' scheme for the *B*—*X* system of MnS (Number in parentheses indicates the visual estimates of intensity).

v' / v	0	1	2	3	4
0	22319.8 (4)	21833.7 (3)	21351.2 (2)		
1	22782.0 (3)	22294.7 (2)			20854.8 (3)
2	23240.3 (1)	22754.9 (2)	22272.1 (2)		
3	23693.6 (1)	23209.0 (1)	22726.5 (1)		

4. Discussion

The thermal emission spectrum of MnS molecule has yielded about 38 bands which have been explained by the proposed analysis. From the distribution of intensity in the

spectrograms (Figures 1 and 2) it is evident that in each case (systems *A* and *B*) the most intense bands lie on a well-formed parabola whose shape conforms to the nature of the vibrational constants of the manganese monosulphide molecule. In view of the above facts and results reported earlier [1-3] it appears that the bands have been rightly attributed to the diatomic MnS.

The ground state vibrational frequency of the MnS molecule has been found to be 490.6 cm^{-1}. As MnS is a heavier molecule belonging to the same molecular group as MnO, the value of its ground state frequency (ω'') is normally expected to be less than the ω_e'' value for MnO. For MnO ω_e'' = 839.6 cm^{-1} [6] while for MnS we have determined its value as 490.6 cm^{-1} which appear justifiable.

The dissociation energy of MnS molecule is given by

$$D_e = \frac{\omega_e''^2}{4\omega_e'' x_e''}$$

Substituting the values, we get D_e = 33428.9 cm^{-1}. This value is quite near to the value reported by Drowart *et al* [7] through their mass spectrometric studies.

The ground state electronic configurations of manganese and sulphur atoms are given by :

$$_{25}Mn = 1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^6, 4s^1 — {}^2S_{5/2}$$

$$_{16}S = 1s^2, 2s^2\,2p^6, 3s^2\,3p^4 — {}^3P_2$$

Consider the separated atoms model, we have manganese with $^6S_{5/2}$ and sulphur with $^3P_2$ as their ground states. The combination of these two atomic states gives rise to $^4\Sigma$, $^4\Pi$, $^6\Sigma$, $^6\Pi$ $^8\Pi$ and $^8\Sigma$ electronic states. In the spectrogram we have identified few atomic lines of manganese. Consider well known four atomic lines *viz.* λ 5341 Å, λ 5394 Å, λ 5432 Å and λ 4754 Å due to Mn which appeared in the thermal emission spectrum under discussion and they are found to arise from excited atomic states ^6P, ^8P ^8P and ^8P respectively. It is therefore believed that the excited states of MnS responsible for these transitions arise from these excited states of manganese. The molecular electronic states arising due to the formation of MnS molecule can be derived by the application of separated atom model considering sulphur atom in its ground state ^3P and manganese atom in its different excited states. From the literature [8] the resultant molecular electronic states are found as;

Atomic states	Molecular states
^6P (Mn) + ^3P (S)	$\Sigma(3), \pi(2), \Delta(1)$
^8P (Mn) + ^3P (S)	$\Sigma(3), \pi(2), \Delta(1)$

Since thermal emission is a low energy process, no intercombination system is expected to appear. It is well established that ground electronic state for MnO molecule is $^6\Sigma$ [6]. Since MnO and MnS are molecule of the same family, we expect MnS to have the same ground state as MnO *i.e.* $^6\Sigma$. If $^6\Sigma$ would be the ground state of MnS molecule then

optically accessible transitions are $^6\Sigma$—$^6\Sigma$ and $^6\Pi$—$^6\Sigma$. Further the observed bands of the A—X and B—X systems are single headed and well developed (intense) therefore both the systems involved transition $^6\Sigma$—$^6\Sigma$. This is also conformed by Doubay *et al* [3] by investigating the rotational structure of (0, 0), (0, 1) and (0, 3) bands of the A—X system using LIF studies.

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